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Template and Guest Effects on the Self-Assembly of a Neutral and Homochiral Helix**

Frank M. Tabellion, S. Russell Seidel, Atta M. Arif, and Peter J. Stang*

Dedicated to Professor Manfred Regitz
on the occasion of his 65th birthday

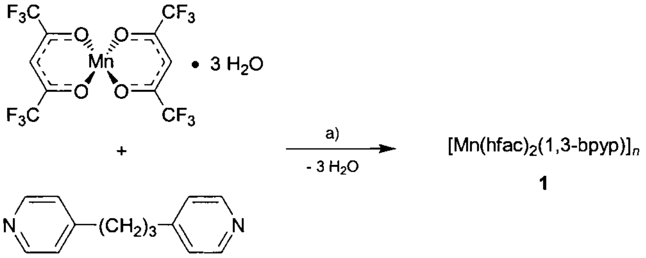
Over the past decade, the principles of recognition-driven, spontaneous self-assembly have become further elucidated. In such processes, the overall structure of the product is controlled by the combination of binding constraints and geometrical requirements. These intriguing discoveries have led to the development of general strategies for the design of abiotic, supramolecular entities, both discrete and infinite, that use coordination as a motif.[1]

The coordination paradigm pioneered by Lehn and Sauvage, and as developed in the groups of Fujita, Raymond, Stang, and others for closed systems, has allowed for the synthesis of a large assortment of supramolecular polygons and polyhedra through "rational design". This approach utilizes rigid subunits that have been pre-coded with the proper bonding and angular information, leading to highly predictable products.[2] Concurrently, a variety of solid-state coordination polymers and infinite-network lattices have been synthesized along similar lines.[1b, 3]

By incorporating a higher degree of flexibility into the building blocks, the amount of predefined information is reduced, and two or more different structures can arise from identical metal–ligand combinations. This strategy yields largely unpredictable products that depend mostly upon minor, experimental variations.[4] The iron-based circular helicates made by Lehn's group[5] and the cadmium-based, flexible coordination networks from Fujita's group,[6] are dependent upon the anion or guest employed, respectively, and serve as impressive examples of this methodology.

The work presented here is concerned with tuning the assembly of a new, neutral, solid-state system and serves as a step toward bridging the gap between discrete and infinite supramolecular structures. Such work may also have implications in crystal engineering.[7] In this study, the solid-state assembly of the highly flexible 1,3-bis(4-pyridyl)propane (1,3-bpyp) ligand and the neutral [Mn(hfac)$_2$(H$_2$O)$_3$] (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) acceptor complex was probed under various reaction conditions.

By slow evaporation of the solvent from a previously heated 1:1 mixture of [Mn(hfac)$_2$(H$_2$O)$_3$] and 1,3-bpyp in acetone/methanol, crystals of **1** were obtained (Scheme 1).



Scheme 1. a) MeOH / (CH$_3$)$_2$CO / Δ.

As determined by single-crystal X-ray analysis,[8] the coordination polymer **1** exhibits a helical architecture in the solid state (Figure 1). This system crystallized in the chiral space group C_2, with two independent manganese centers per repeating asymmetric unit. Both pseudo-octahedral metal centers show *cis* coordination of the pyridine moieties and are enantiomeric. Each set of two crystallographically equivalent manganese centers constitutes a single revolution of the helix with a distance of 19.18 Å between them.

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[*] Prof. Dr. P. J. Stang, Dr. F. M. Tabellion, S. R. Seidel, Dr. A. M. Arif
Department of Chemistry
University of Utah
315 S. 1400 E. RM 2020 Salt Lake City, UT 84112 (USA)
Fax: (+1) 801-581-8433
E-mail: stang@chemistry.utah.edu.

[**] This research was supported by the National Science Foundation (CHE-9818472) and the Alexander von Humboldt Foundation through a Feodor Lynen Fellowship for F.M.T.

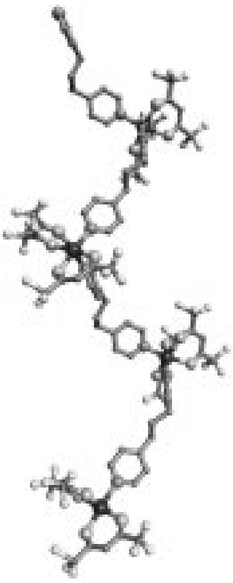


Figure 1. A segment of helical polymer **1**.

Typically, helical systems arising from achiral starting materials show an equal distribution of *P*- and *M*-helices, making them overall racemic.[9] In this case, however, crystals that grew from a single point of nucleation exhibited spontaneous self-resolution into homochiral entities.[10] In any given batch, multiple nucleation points led to apparently random distributions of left-handed and right-handed crystals.[11] From careful study of the crystal packing diagram of **1**, we assume that the resulting homochirality of any particular single crystal arose from the interlocking of the hfac trifluoromethyl groups between the turns of adjacent helices as the system crystallized (Figure 2).

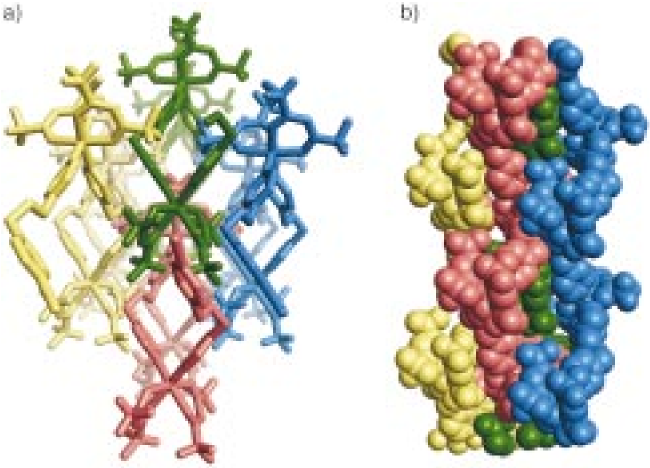
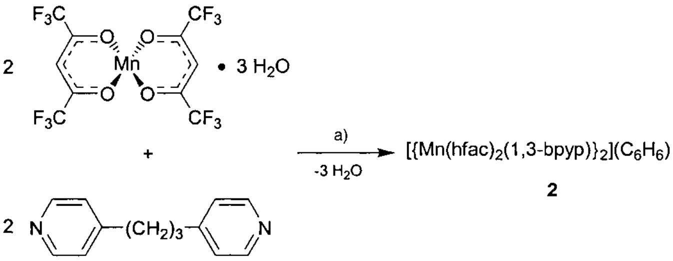


Figure 2. Representation of the crystal packing in compound **1**: a) View of **1** along the helical axis, showing the interlocking of the helices. b) Side view of **1** as a space-filling model. Protons are omitted for clarity.



Scheme 2. a) MeOH / $(CH_3)_2CO$ / C_6H_6 / Δ; recrystallization in the presence of C_6H_6.

A slight variation in the reaction conditions, such as crystallization in the presence of benzene, induces a dramatic effect on the solid state structure of **1**. Instead of crystallizing as an infinite helical polymer, a closed, inorganic cyclophane **2** is formed (Scheme 2). This assembly consists of two independent, enantiomeric manganese centers bridged by two 1,3-bpyp ligands, with the metals having the same coordination geometry as seen for those in **1**. As determined by single-crystal X-ray analysis,[12] the cross-ring, manganese–manganese separation is 10.4 Å, and the shortest carbon–carbon, cross-ring separation is 6.5 Å (Figure 3).

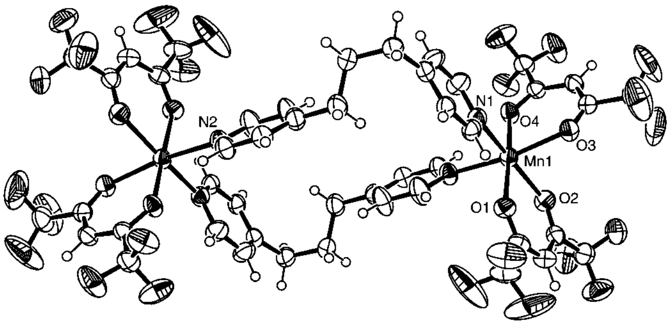


Figure 3. ORTEP drawing of the molecular structure of cyclophane **2**.

The crystal packing diagram for **2** clearly reveals that the cocrystallized benzene molecules act as templates in the formation of the ring system, suppressing any oligomerization that may occur (Figure 4). The stacking of these entities leads to the formation of intermolecular channels. The benzene molecules sit above and below the planes of **2** and do not occupy the internal cavities, which leads to the formation of alternating, sandwichlike sheets, with an inter-sheet, manganese–manganese separation of 10.3 Å.

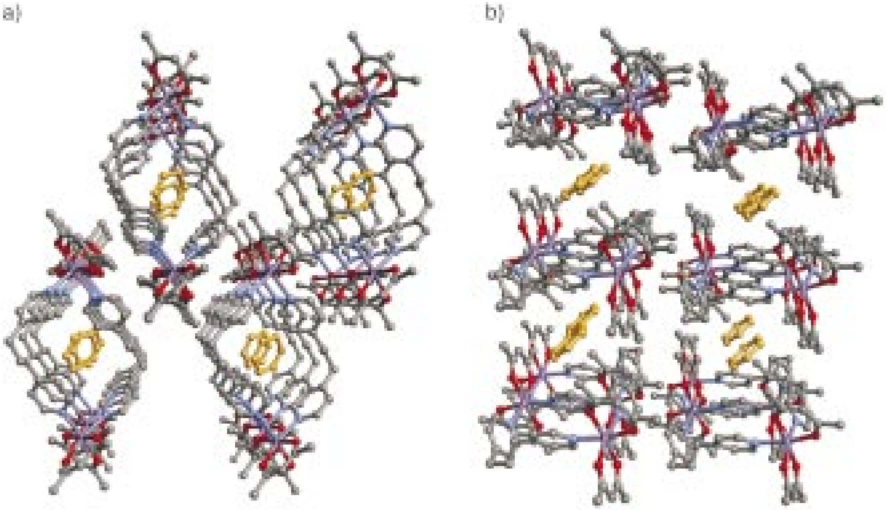
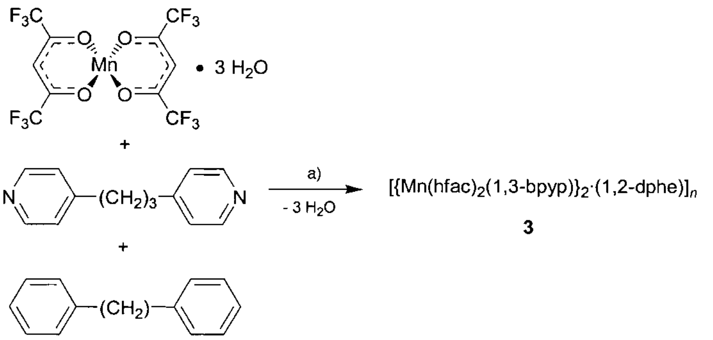


Figure 4. Crystal packing illustration of cyclophane **2**. a) Perspective view of the intermolecular channels of **2**. b) Side view showing the alternating, sandwich-like sheets of **2**. Protons and fluorine atoms omitted for clarity.

An X-ray analysis reveals that **1** acts as a host compound if the crystals are grown in the presence of 1,2-diphenylethane (1,2-dphe; Scheme 3).[13] However, in contrast to **2**, the helical structure of **1** remains intact. Each coil of the helix includes two residues as in **1** (Figure 5). Despite these similarities, the guest molecule has a significant impact on the solid-state structure of **3**. For instance, the distance between the coils (10.3 Å) is considerably smaller than in **1**. Furthermore, the conformation of the coordinated 1,3-bpyp ligand changes in going from **1** to **3**, resulting in the latter having an augmented internal cavity volume per unit cell. In addition, **3** crystallizes in the achiral space group $P2_1/n$, and accordingly both *P*- and *M*-helices are present in equal amounts (Figure 6). We believe that this occurs as a result of the 1,2-dphe guest effectively filling the helical cavity and preventing the aforementioned interlocking of adjacent helices. Interestingly, a recognition phenomenon between the host and 1,2-dphe guest molecule occurs, with the host forcing the guest into an unfavorable, nearly eclipsed, *syn* conformation. A detailed examination of the crystal structure did not reveal an obvious interaction between the host and guest.



Scheme 3. a) MeOH / $(CH_3)_2CO$ / Δ.

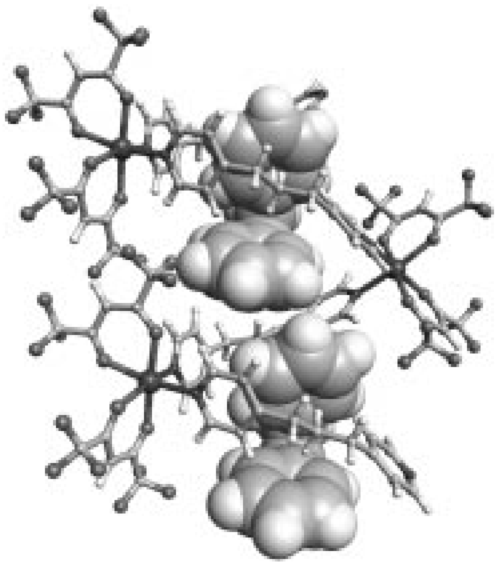


Figure 5. A section of helical polymer **3**, with the 1,2-dphe guest molecules shown as a space-filling model.

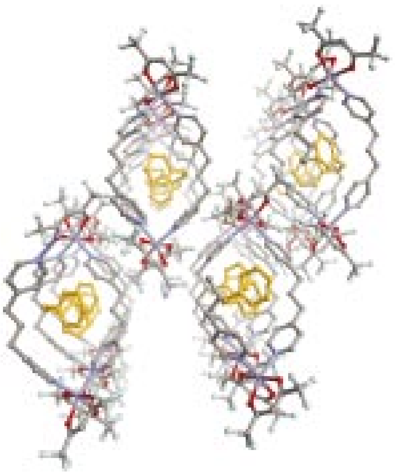


Figure 6. Crystal packing diagram of polymer **3** along the helical axis. Protons omitted for clarity.

In conclusion, the condition-dependent solid-state assembly of self-templated homochiral complex **1**, determined here by single-crystal X-ray analysis, can be tuned by varying the template or guest present. This effect results in solid-state products ranging from closed dinuclear assemblies **2** to racemic mixtures of infinite helices **3**. In addition, each of these supramolecular species are electronically neutral. To the best of our knowledge, this complex–ligand combination represents a unique case in which the supramolecular assembly can be synthesized in the presence of a template, a guest, or without either and exhibits drastic structural differences depending on the method used. This feature aids in bringing together the two fields of discrete and infinite supramolecular structures and may have implications in the area of crystal engineering.

Experimental Section

1: $[Mn(hfac)_2(H_2O)_3]$ (1 equiv) and 1,3-bpyp (1 equiv) were placed in a mixture of methanol/acetone. The resulting solution was heated for 0.5 h during this time it became slightly darker yellow. Crystals of **1** were grown out of this solution by slow evaporation of the solvent in 87.2% yield; elemental analysis, calcd (%) for $Mn_1C_{23}H_{16}N_2O_4F_{12}$: C 41.40, H 2.42, N 4.20; found: C 41.59, H 2.46, N 4.29.

2 and **3** were produced under the same reaction conditions as **1**, except the crystallization was carried out in the presence of benzene and 1,2-dphe, respectively. Product **2** was obtained in 96.9% yield, **3** in 73.8%; elemental analysis, calcd (%) for **2** $Mn_2C_{46}H_{32}N_4O_8F_{24} \cdot C_6H_6$: C 44.21, H 2.71, N 3.97; found: C 42.88, H 2.67, N 4.17 (note: the C value in the elemental analysis for **2** is low because of the loss of lattice benzene molecules during the drying and elemental analysis processes); elemental analysis, calcd (%) **3** $Mn_2C_{46}H_{32}N_4O_8F_{24} \cdot C_{14}H_{14}$: C 47.51, H 3.06, N 3.69; found: C 48.13, H 3.19, N 3.72.

Received: November 17, 2000 [Z16124]

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[8] Crystal structure analysis of **1** at 200(1) K: $C_{46}H_{32}N_4O_8F_{24}Mn_2$, $M_r = 1334.64$, yellow prism, $0.33 \times 0.25 \times 0.08$ mm, monoclinic space group C_2, $a = 20.5454(7)$, $b = 11.7067(4)$, $c = 12.7161(5)$ Å, $\alpha = 90$, $\beta = 114.4019(18)$, $\gamma = 90°$, $V = 2785.25(15)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.591$ g cm^{-3}, $Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å, $\mu = 0.586$ mm^{-1}. Data were collected on a Nonius KappaCCD diffractometer in the range $3.90 < 2\theta < 30.07°$. A total of 6949 measured reflections, 6949 unique, 4951 with $F_0^2 > 4\sigma(F_0^2)$ were used to refine 536 parameters to $R1(wR2) = 0.0501(0.1037)$, GOF = 1.011, F^2 refinement in SHELXL97. A multiscan absorption correction gave min. and max. transmission factors of 0.9546 and 0.8301. The residual peaks in the final difference map ranged from -0.229 to $+0.707$ e Å^3. All four CF_3 groups are disordered in two different orientations with a nearly 50:50 occupancy. The 1,3-bpyp ligand was found also to be disordered in two slightly different orientations with a major orientation of 70%.[14]

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[11] Several crystals of different product batches showed, by circular dichroism (CD) spectroscopy, the apparently random distribution of *P*- and *M*-helices.

[12] Crystal structure analysis of **2** at 200(1) K: $C_{52}H_{38}N_4O_8F_{24}Mn_2$, $M_r = 1412.74$, yellow prism, $0.23 \times 0.20 \times 0.20$ mm, triclinic space group $P\bar{1}$, $a = 10.2719(7)$, $b = 12.9946(9)$, $c = 13.0612(7)$ Å, $\alpha = 61.494(4)$, $\beta = 83.550(4)$, $\gamma = 81.017(3)°$, $V = 1511.82(17)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.552$ g cm^{-3}, $Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å, $\mu = 0.545$ mm^{-1}. Data were collected on a Nonius KappaCCD diffractometer in the range $2.50 < 2\theta < 26.02°$. A total of 8635 measured reflections, 5881 unique, 4488 with $F_0^2 > 4\sigma(F_0^2)$ were used to refine 407 parameters to $R1(wR2) = 0.0565(0.1342)$, GOF = 1.039, F^2 refinement in SHELXL97. A multiscan absorption correction gave min. and max. transmission factors of 0.8989 and 0.8849. The highest peak in the final difference map ranged from -0.436 to $+0.604$ e Å^3.[14]

[13] Crystal structure analysis of **3** at 200(1) K: $C_{60}H_{46}N_4O_8F_{24}Mn_2$, $M_r = 1516.89$, yellow prism, $0.25 \times 0.23 \times 0.20$ mm, monoclinic space group $P2_1/n$, $a = 10.2946(1)$, $b = 28.1849(5)$, $c = 22.6755(5)$ Å, $\alpha = 90$, $\beta = 98.3108(10)$, $\gamma = 90°$, $V = 6510.25(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.548$ g cm^{-3}, $Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å, $\mu = 0.512$ mm^{-1}. Data were collected on a Nonius KappaCCD diffractometer in the range $2.20 < 2\theta < 26.05°$. A total of 22624 measured reflections, 12755 unique, 7936 with $F_0^2 > 4\sigma(F_0^2)$ were used to refine 1003 parameters to $R1(wR2) = 0.0576(0.1186)$, GOF = 1.022, F^2 refinement in SHELXL97. A multiscan absorption correction gave min. and max. transmission factors of 0.9045 and 0.8827. The residual peaks in the final difference map ranged from -0.347 to $+0.318$ e Å^3. Four CF_3 groups were disordered in two different orientations with partial occupancy ranging from 0.75 to 0.92. The 1,2-dphe molecule was also disordered in two slightly different orientations with a major orientation of nearly 60%.[14]

[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153290, CCDC-153291, and CCDC-153292. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Ultrafast Electron Diffraction of Transient [Fe(CO)$_4$]: Determination of Molecular Structure and Reaction Pathway**

Hyotcherl Ihee, Jianming Cao, and Ahmed H. Zewail*

Transition metal carbonyl complexes[1, 2] respond to ultraviolet light by the loss of one or more CO ligands and subsequent formation of coordinatively unsaturated carbonyl complexes, which are known to catalyze a variety of reactions.[3–5] The photochemistry governing the formation of these coordinatively unsaturated species has been an active area of research both experimentally[6–13] and theoretically,[14–19] often focusing on the reaction pathways and molecular structures of these transient species. Among transition metal carbonyl complexes, [Fe(CO)$_5$] is one of the most extensively studied molecular systems. [Fe(CO)$_5$] absorbs strongly in the ultraviolet starting at about 350 nm (3.5 eV).[18, 20–22] The spectrum is rather featureless, and is dominated by metal-to-ligand charge transfer transitions[18] at high energies. Having five carbonyl ligands, an [Fe(CO)$_5$] molecule can dissociate into five different products ([Fe(CO)$_x$], $x = 4, 3, 2, 1, 0$) depending on the excitation wavelength.

In these reactions, [Fe(CO)$_4$] is the primary intermediate and serves as a "doorway" molecule for various subsequent reactions,[23, 24] such as decomposition, recombination with the carbonyl ligand, and coordination with solvent molecules. Elucidating the nature of [Fe(CO)$_4$], including its electronic states and the corresponding molecular geometry, is important for understanding the role of intermediates in the photolysis of transition metal carbonyl complexes.

Herein we report the direct determination of the molecular structure (Figure 1) of transient [Fe(CO)$_4$] using diffraction with ultrashort pulses of electrons. In this way, we are able to identify the primary reaction pathway and provide details of

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[*] Prof. A. H. Zewail, H. Ihee, Dr. J. Cao[+]
Laboratory for Molecular Sciences
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, CA 91125 (USA)
Fax: (+1) 626-796-8315
E-mail: zewail@caltech.edu

[+] Present address: National High Magnetic Field Laboratory
Florida State University
1800 East Paul Dirac Drive
Tallahassee, FL 32310 (USA)

[**] This work was supported by grants from the National Science Foundation, Air Force Office of Scientific Research, and the Office of Naval Research.